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Bioiesel Washing For Acceptable Quality Standard

Nnorom Achara and, NCOzoekwe,
Nigerian Defence Academy, Kaduna, Nigeria
Corresponding Author Nnorom Achara

ABSTRACT:*Inthe production of biodiesel, methanol is usually the alcohol of choice. In this process, in order to ensure complete reaction, excess methanol over the stochiometric requirement is used. For quality specification, the excess unreacted methanol has to be removed together with the other contaminants: free glycerine, soap and water. Methanol however is a dangerous material to handle therefore appropriate precaution should be taken for personnel safety. Two broad techniques are available for the purification of biodiesel – water washing and waterless cleaning (ion exchange method). The water wash include Stir wash, Bubble wash and Film wash. Performance of engines using unwashed biodiesel will gradually deteriorate and end up with corroded fuel lines. In biodiesel production and use there are two other pitfalls to avoid which are emulsification and polymerisation.*

KEYWORD*: transesterification, monoglyceride, diglycerides, triglyceride, polymerisation, emulsification*.

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I. INTRODUCTION

Biodiesel is made by reacting a triglyceride (a component of oil or fat) with an alcohol to produce methyl ester, usually with the aid of a catalyst (such as sodium methoxide). It can be produced from many different alcohols but methanol is the simplest, most reactive and least expensive of all the alcohols, which makes it the material of choice for biodiesel production. However, it is more dangerous to handle and store than some of the heavier alcohols, such as ethanol [1]. Most of the biodiesel production methods require an excess of the alcohol, methanol usually over the stoichiometric ratio required for the reaction. Typically, an excess of twice the required amount is used. In the production, there is the possibility of reversible reaction and again because of the peculiar nature of the equilibrium, the use of excess methanol is necessary to achieve a more complete reaction for a high quality product. The presence of the excess methanol after reaction is unwanted and therefore constitutes a contaminant that has to be removed together with the other contaminants [2]. Because of these contaminants, after producing the methyl esters, the biodiesel needs to be purified before the fuel is suitable for use in engines. In addition to the methanol, the fuel is likely to contain soap, free glycerine and water, all of which are required to be removed. The purification process is aimed at meeting the national quality specification for example (ASTM D 6751), and hence to provide trouble-free operation in the engine [3].

At the biodiesel purification stage, relying on allowing the product to freely settle followed by filtering will not remove the soap, catalyst, glycerine and the excess methanol contaminants. Although methanol is also a fuel, it is only acceptable in specially engineered racing cars. The performance of a diesel engine using biodiesel containing excess methanol will gradually deteriorate as the fuel will eventually corrode the fuel injection system. Some large scale manufacturers appear to believe that the problem is peculiar to small scale manufacturers [4-8] . However, this can only be viewed as a prejudice against the small scale brewers, if the biodiesel is not well made in the first place, it will fail to separate after washing and this has nothing to do with the size of the manufacturing facility. It is however a known fact that oil and water do not mix easily, therefore well-made biodiesel should separate quickly and cleanly from the wash water when it settles. Badly produced biodiesel on the other hand will contain half-processed oil molecules - monoglycerides and diglycerides and these are emulsifiers. Stable mixtures of oil and water, for example mayonnaise, are made using emulsifiers. An indication of emulsion problem is given if after washing, the biodiesel-water mixture fails to separate or separates slowly. If it does not separate, the processing needs to be improved. Properly made biodiesel with good reaction to completion will not emulsify. No water wash method should be used on any batch unless it is known for certain that the batch has reacted to completion.

The purpose of this study is to look at the various purification techniques that when adopted will make the biodiesel meet the desired quality specification.

II. PURIFICATION METHODS

Various techniques have been developed for purifying the resulting biodiesel. The two broad methods are the water and the waterless purification techniques [3,9]. There is also the ultra-sound assisted production technique which on its own cannot be classified as a purification group since its only contribution is to make the biodiesel production faster [10].

2.1 Water Washing Types

The water washing can be divided into three methods namely stir washing, mist washing and bubble washing.

2.1.1 Stir Washing

Stir washing involves mixing thoroughly the resulting contaminated biodiesel with water to a high homogenous level using preferably a motor driven impeller. After stirring and mixing for about five minutes, the mixture is allowed to settle for about another one hour and then the water is drained from the bottom. The process is repeated for about two times. The biodiesel is either allowed to air-dry or heated to 48^{oC} for the same purpose. Stir washing works only if the reaction is complete else emulsion problem results,fig. 1.

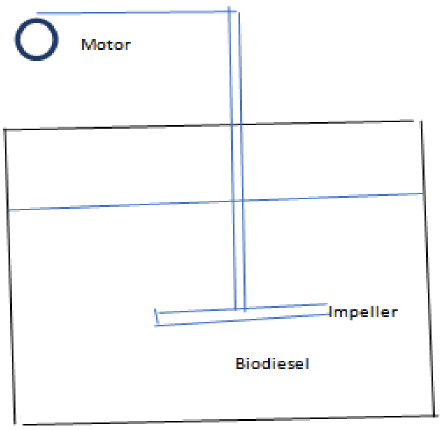

Fig.1 Schematic Arrangement for Stir Washing

2.1.2 Mist Washing

In Mist-washing a fine spray of water is introduced at the top of the wash-tank to send a mist of water droplets down onto the surface, creating zero agitation. It works but it is slow and uses a lot of water which is not usually re-used, fig.2. The water droplets carry the contaminants as they travel down the wash-tank.

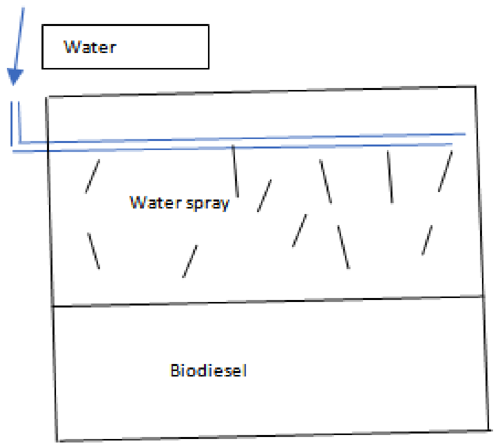

Fig.2 Schematic Arrangement for Mist Washing

2.1.3 Bubble Washing

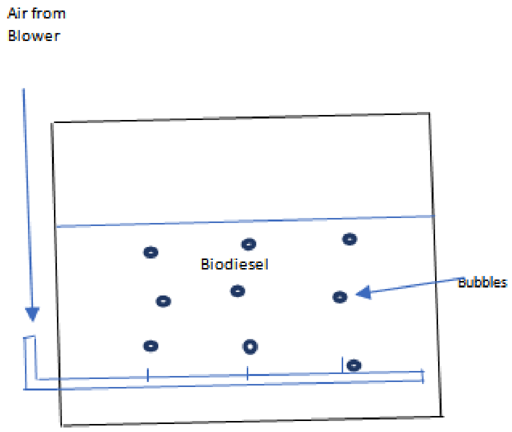

Fig.3 Schematic Arrangement for Bubble Washing

Bubble-washing was developed at the University of Idaho. It uses a small air-pump and bubble-stones. Water is added to the biodiesel in the wash tank (usually a quarter to half as much water as biodiesel); the water sinks to the bottom. The bubble-stones are also thrown in and these also sink to the bottom. The air pump is switched on. Air-bubbles (best to create lots of little bubbles) rise through the water and into the biodiesel, carrying films of water around and these wash the biodiesel around the bubbles. When the bubble reaches the wash tank surface it bursts, leaving the water to sink back down again, washing the fuel a second time, fig. 3.

Usually three to four washes are required, each of six to eight hours duration, often less for the first wash, with a settling period of at least an hour between washes. After it has settled the water is removed via a bottom-drain and replaced with fresh water. The washing is complete when the water is clear after settling, with a pH of 7 (or the same as the tap-water). Care should be taken in choosing the air-bubble stones because some are not biodiesel-proof as they crumble immediately after first use. Ceramic stones can last indefinitely and rough-gradecarborundum stone is also known work well. The bubble wash does not require much effort but a lot of time. The bubble-washing is gentle and as such can mask an incomplete reaction, which agitation will reveal immediately.

2.2 Waterless Wash - Ion Exchange

Waterless methods of purifying biodiesel have been introduced into the marketplace, such as ion exchange resins and synthetic magnesium silicate. A number of different companies manufacture ion exchange resins (small polymer beads) to clean biodiesel. Although the products are similar, the description of the principle under which the products work are sometimes very different. For example, one group says the beads work by exchanging ions (the sodium or potassium ions from the soap in the biodiesel are exchanged with hydrogen ions on the bead surfaces). On the other hand, the other group, claims that the cleaning is accomplished via glycerine and soap interaction. However, the University of Idaho has conducted a series of experiments on ion exchange resins to determine how they work, including how long they remain effective and has concluded that each of these claims may be contributing to the overall cleaning process [9].

III. DISCUSSION

Safety considerations are necessary in the use of methanol, CH_3OH, a colourless liquid that is highly volatile (boiling point of 64.7°C) and flammable (flash point of 8ºC), which when it burns produces an invisible flame. It is very toxic and quickly absorbed into the body through the skin and lungs when exposed to the liquid and/or the vapour. Appropriate safety precautions must be taken to avoid accidents [1]. In order to improve efficiencies, conserve resources and reduce cost, producers factor in the recovery and reuse of the excess or residual methanol. This alcohol is distributed between the lighter biodiesel phase and the heavier glycerol phase, the by-product. The phases are separated by gravity, centrifugation or some other method is used for the methanol recovery process. Sometimes a partial recovery is effectively made before separation. Some of the methods used to recover methanol as part of the biodiesel production process, as well as how to refine it for reuse are detailed in [11].Recovery methods vary greatly depending on the production processes and throughput.

It has been hypothesized that the ion exchange resins might work in four different ways. The beads are presumed to work via ion exchange: they exchange a hydrogen ion with the sodium or potassium ion in the soap. Another possible method of cleaning involves filtration. The ion exchange bead can act as a filter. If soap and glycerine have precipitated from the solution, which they are prone to do when the cosolvent methanol is removed, the soap and glycerine can be removed by simple filtration. Adsorption is a third possible cleaning mode. Adsorption occurs when polar contaminants attach themselves to the bead surface due to the attraction of intermolecular forces. In fact, synthetic magnesium silicate, another popular waterless method of cleaning biodiesel, is known to work through adsorption: binding the polar soap or glycerine molecules to its surfaces. The fourth possible mode of cleaning is the soap-glycerine interaction. Glycerine is thought to be removed from biodiesel through adsorption or filtration. Glycerine being a highly polar molecule, is held on the surface of the adsorbent by attraction to polar groups already on the surface. Soap, being soluble in glycerine, would be dissolved into the glycerine and removed from the biodiesel with it.

The study at the University of Iowa showed that at lower soap levels (less than 1,000 ppm), the beads works almost completely through ion exchange. At higher soap levels, the beads works mostly through ion exchange, but not entirely. Other modes of cleaning appear to be operating at these high soap levels—possibly a combination of the other three modes. Glycerine is not removed through ion exchange at all, since there are no relevant ions to exchange. Instead, glycerine removal probably happens through adsorption and filtration. For example, the precipitated soap material that collects at the bead surface also contains glycerine and trapped biodiesel. Contrary to the claim by some manufacturers, the Idaho study showed, instead, that the products had a gradual decline of effectiveness. As one mode of operation stopped working (such as ion exchange), other modes continued to work (such as filtration, or soap and glycerine interaction). Therefore, the products did not show a sudden drop in effectiveness. Rather, the effectiveness gradually declined until the soap or glycerine levels exceeds the specification limits. The tests also found that a higher soap level caused the beads to lose their effectiveness more quickly.

Water washing perhaps provides one of the best-known purification techniques used by biodiesel producers, especially at the small-scale level. Even though no survey results are found in the literature, it is often the preferred option. Except in distillation, all the techniques used to purify biodiesel rely on the difference in molecular polarity between the methyl esters in biodiesel and the contaminants. Methanol, soap, and glycerine are all polar and are thus strongly attracted to each other and polar solvents such as water. Methyl esters are only slightly polar and thus have limited solubility in water and with the contaminants. Depending on the temperature, only about 4-6% methanol is soluble in methyl esters, [5]. Frequently, multiple cycles of washing are required to achieve sufficiently low levels of the contaminants. Some producers have argued against water washing sighting the need to minimize water wastage, possibility of emulsion formation and the complication of handling methanol dissolved in water. In recognition that water is a commodity that may be in short supply, plant designs are available that recycle the water within the plant so as to minimize waste-water discharge.

Perhaps the most frustrating aspect of water washing is the formation of emulsions between the water and the methyl esters. Soap and monoglycerides seem to be the most prominent surfactants that stabilize these emulsions. Emulsions due to soap seem to be shorter-lived while emulsions created by an excess of monoglycerides may be permanent. If emulsions occur, they can usually be broken with the addition of acid, but the resulting product will usually require reprocessing. To use water washing effectively requires that free fatty acid (FFA) and water levels of the incoming oil feedstock be as low as possible to minimize soap formation during the transesterification process. FFA less than 0.5% and water less than 0.1% is desirable. Water washing requires that initial washing steps be conducted with a minimum of agitation and without air entrainment to prevent emulsion formation. Later wash stages can be more vigorous when soap levels are lower (< 1000 ppm).

While water washing can be troublesome, it is a robust technique that uses no costly materials, handles high contaminant levels, and produces biodiesel that meets all requirements of the ASTM specification. If patience and proper care are taken, it can be executed with minimal problems even in high volume production environments. Water washing has an important advantage over ion exchange resins. If some process upset occurs in the plant, such as a pump failure or a feedstock quality variation, depending on the process route, production cost can become very high. If this material is supplied to a bed of ion exchange resin, it can overwhelm the active sites on the resin beads and exhaust the entire bed requiring very expensive replacement. So, a mistake that might have just cost a few hours of production could end up costing much more.

Ion exchange resins are small plastic beads coated with a material that attracts polar compounds such as glycerine and soap. The beads are more expensive than the adsorbents, but they can be used for product batch runs and can be regenerated to restore glycerine removal by washing with methanol although regeneration for soap removal is more complicated and is generally not performed at the plant level. Distillation is becoming popular but it should also be noted that distillation does not eliminate the need for purification because while the process removes monoglycerides and soap, free glycerine has boiling properties that are close enough to those of methyl esters that it will not be removed by distillation. Although most free glycerine is removed by settling tanks or centrifugation, the amount that remains with the methyl ester, either dissolved or as small droplets, exceeds the allowable specification of 0.02%. This free glycerine must be removed before distillation by either water washing, adsorbent, or by an ion exchange resin

Similarly, to minimize monoglycerides residue in the finished fuel requires a good quality reaction. This means adequate time and temperature as well as sufficient catalyst and excess methanol.

The use of a dilute acid mixed with the wash water can also help to minimize emulsion formation. However, strong acids will split the soap back to a salt and FFA, and when the soap level is high (> 2500 ppm), the resulting acid value will exceed the level allowed by the ASTM specification.

3.1 Oxidation and Polymerisation

A more complicated problem with bubble-washing is fuel oxidation.The composition and properties of various oil feed-stocks are different. Some are 'drying' oils, for example linseed oil and that is why it is used in paints and varnishes. When it dries the oil irreversibly polymerises into a tough, insoluble, plastic-like solid. At high temperatures found in diesel engines the process is accelerated to result in steadily accumulating films of tough, insoluble, plastic-like solids which are undesirable in the engine and injector pump.

Polymerisation occurs when the double bonds in unsaturated oil molecules are broken by oxygen from the air or water. The oil oxidises, forming peroxides (hydroperoxides), and the peroxides polymerise, bonding with carbon to create a long and stable molecule called polymer (plastic). Another effect of oxidation is that the hydroperoxides attack elastomers, such as pump seals.Without oxygen the oil cannot polymerise. Oxidation and polymerisation do not only affect the drying oils, there are also semi-drying oils, many of which are commonly used to make biodiesel, including sunflower and soy.Saturated oils don't polymerise, unsaturated oils do. The level of unsaturation is called the Iodine Value (IV), the higher the IV, the more unsaturated the oil, the faster it will oxidise and polymerise. Linseed oil, tung oil and some fish oils have IVs of between 170 and 185. Coconut oil on the other hand, has an IV of 10 and won't polymerise. Converting unsaturated oils to biodiesel lessens the polymerising effect but doesn't prevent it [12].

IV. CONCLUSION:

The study has identified that there are two broad methods for the purification of biodiesel and that water washing is cheaper compared with waterless washing. The drawback of water washing is product emulsification which occurs when the levels of monoclycerides and diclycerides are high. Feedstocks with high iodine value (IV) are candidates for polymerisation.

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